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(54) **Defoliation compositions**

(57) Defoliation compositions for the defoliation of crops such as potatoes, hemp, alfalfa, rape, flax, tomatoes, soya beans, peppers, peas, sunflower, cereals, clover, cotton, vines and sesame, as well as for general defoliation in nurseries and of trees, comprise a defoliating aggregate amount of

a) a herbicide

and b) an activating amount of a solvent as used in the metallurgic industry for the extraction of metals.

GB 2 022 070 A

SPECIFICATION

Defoliation compositions

The present invention relates to a novel method and to compositions for the defoliation of crops such as potatoes, hemp, alfalfa, rape, flax, tomatoes, soya beans, peppers, peas, sunflower, cereals, clover, cotton, vines and sesame, as well as for general defoliation in nurseries and of trees.

In the mechanised harvesting of cultivated foliating crops, there is a considerable demand for an efficient agent which acts to remove the foliage of the crop to avoid fouling of mechanised parts and facilitate harvesting, yet leaves the plant otherwise unharmed.

Accordingly, the present invention provides a method of defoliating crops which comprises applying to the crops a defoliating aggregate amount of

a) a herbicide

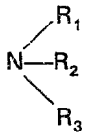
and b) an activating amount of a solvent as used in the metallurgic industry for the extraction of metals.

Preferred herbicides are herbicide phenyl ureas particularly 3-(3-chloro-4-methoxyphenyl)-1,1-dimethyl urea, 3-(3-chloro-4-methylphenyl)-1,1-dimethyl urea and 3-(3,4-dichloro-phenyl)-1,1-dimethyl urea and herbicide triazines particularly 2-chloro-4-ethylamino-6-isopropyl amino-*s*-triazine and 2-chloro-4,6-bis(ethylamino)-*s*-triazine.

Particularly preferred herbicides are the phenyl ureas and especially 3-(3-chloro-4-methoxyphenyl)-1,1-dimethyl urea (Metoxuron).

Solvents used in the metallurgic industry for the extraction of metals hereinafter referred to as activators may be mainly classified in two general groups

i). one group comprising amines of formula I



I

wherein R_1 and R_2 are each, independently, a C_{1-24}hydrocarbon group

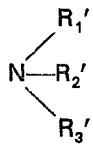
and R_3 is hydrogen or a C_{1-24}hydrocarbon group,

ii). a second group comprising plasticizers for polymers.

In case the activator is an amine of formula I, it is preferably a tertiary amine and more preferably a symmetrical tertiary amine, i.e. in which R_1, R_2 and R_3 are identical.

Each hydrocarbon group may be aromatic, alicyclic or aliphatic, preferably the latter. Preferably the aggregate of R_1, R_2 and R_3 contains C_{15-60}, more preferably C_{15-45} particularly C_{15-36} especially C_{21-36}.

Preferred amines are the compounds of formula I*a*,



I*a*

wherein R_1', R_2' and R_3' are each, independently, C_{6-20}, more preferably C_{6-12}, particularly C_{6-9}, alkyl.

The amine may be employed in free base, in agriculturally acceptable ammonium or in quaternary ammonium salt form. By "agriculturally acceptable ammonium or quaternary ammonium salt form" is meant those ammonium or quaternary ammonium salt forms which exhibit sufficient stability for agricultural use. Examples of such ammonium salts are the phosphate, pyrophosphate, polyphosphate, phosphonate, phosphite, sulphate and sulphite. The preferred ammonium salt is the phosphate. The preferred quaternary ammonium salt form is the methylammonium chloride.

Especially preferred amines are tri-n-hexyl amine, tri-caprilyl amine and tri-n-octyl amine in free base or agriculturally acceptable ammonium or quaternary ammonium salt form, e.g. in phosphate or methylammonium chloride form.

The most preferred amine is tri-*n*-octyl amine in free base or agriculturally acceptable ammonium salt form, e.g. phosphate form.

The term "plasticizer for polymers" is employed in the polymer art to designate an agent which is added to a polymer to facilitate processing of the polymer or to modify the service properties of polymers.

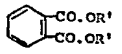
Plasticizers for polymers which have been found to be of particular interest as defoliant activators are aliphatic or aromatic esters particularly aliphatic or aromatic esters of carboxylic acids or of phosphoric acid, and especially compounds of formula II,

$$(RO)_x—A \qquad II$$

wherein each R is independently C_{1-12}alkyl, C_{2-12}alkoxy-alkyl or phenyl,
A is an acyl residue of any aliphatic or aromatic carboxylic acid or of phosphoric acid,
and x is an integer 1 to 3 being the number of free valencies of the phosphoric acid ester or the carboxylic acid residue.
Preferably R is C_{1-12}alkyl, particularly C_{3-6}, especially C_4alkyl.
Particular plasticizer groups of interest are the compounds of formula II*a*

$$(RO)_{3-y}—P(=O)—(OH)_y \qquad IIa$$

wherein R is as defined above,
and y is 0, 1 or 2,
the compounds of formula II*b*,



IIb

wherein R′ is C_{1-12}alkyl,
the compounds of formula II*c*

$$R_4—CO.OR' \qquad IIc$$

wherein R_4 is a C_{8-20} saturated or unsaturated hydrocarbon,
and R′ is as defined above,
the compounds of formula II*d*,

$$(CH_2)_8(CO—OR')—CO—OR' \qquad IId$$

wherein R′ is as defined above,
and the compounds of formula II*e*,

$$CH_2(—CO—OR')—C(OH)(—CO—OR')—CH_2—CO—OR' \qquad IIe$$

wherein R′ is as defined above.

Further interesting activators for use in the method according to the invention and not embraced by the general groups i) and ii) are especially 4-n-nonyl-phenol and tri-n-octylphosphin oxide. (Applied and Environmental Microbiology, vol. *32* (1976), p. 102—107).

The most preferred plasticizer for use in the method of the invention are tri-n-butylphosphate, tri-butoxyethylphosphate and di-(2-ethylhexyl)phosphoric acid.

The defoliating method according to the invention is preferably applied in a weight ratio activator:herbicide in the range of 0.5—5:0.5—4, more preferably 0.25—8:1. When an activator of formula I is used, the weight ratio of activator:herbicide is particularly in the range 1—3:0.5—2. When a plasticizer for polymers, 4-n-nonylphenol or tri-n-octylphosphin oxide is used as an activator, the weight ratio of activator:herbicide is particularly in the range of 0.5—5:1, especially 2—5:1 respectively.

The herbicide aggregate action of the herbicide/activator system according to the invention is such as to effect relatively rapid defoliation without undue damage to the plant.

The herbicide/activator system according to the invention may be employed in commercially available formulation form and applied e.g. as a tank mix or separately. These herbicide mixtures or formulations also form part of the present invention.

In general, the concentrate forms of formulation, which are also provided by the present invention, contain between 1 and 95% by weight of the mixture activator/herbicide, preferably between 25 and 85% by weight of active agents.

The activator is preferably used in the form of a suitable formulation, e.g. an emulsifiable concentrate containing between 25 and 85% of an activator in admixture with an emulsifier and optionally additional solvents and surfactants.

The formulations may be produced in a manner known per se, e.g. by mixing the active agents, optionally with a carrier and other formulating ingredients.

The dosage ratio at which each of the components is applied will naturally vary depending on varying factors, particularly the plant, the herbicide and the activator involved.

In general, however, satisfactory results are obtained when the herbicide/activator system according to the invention is applied so as to yield an application rate of 0.5 to 4, preferably 0.5 to 2 kg of herbicide per hectare of crop.

In the case of, for example, the herbicide Metoxuron in potatoes, generally the herbicide/activator system is applied so as to yield an application rate of 0.5—3 preferably 1—2 kg of Metoxuron per hectare of crop.

The method as well as the compositions according to the invention are particularly useful in the defoliation of cotton, potatoes, hemp and leguminous fodder crops such as alfalfa, in particular of potatoes.

The invention is illustrated by the following examples. Parts are by weight.

EXAMPLE 1

A mature potato crop is treated with a tank mix comprising Metoxuron in the form of Purivel (Trade Mark), an 80% by weight wettable powder commercially available from Sandoz Ltd., Basle, Switzerland, and one of the following commercially available activators in the weight ratios of 2:1 and 4:1 activator:Metoxuron respectively. The activator is used in the form of a suitable formulation, e.g. an emulsifiable concentrate. The tank mix is applied as a foliar spray at a spray rate of 1 and 2 kg/hectare Metoxuron 14 days before normal harvesting. By way of comparison, a similar plot is treated with the same dosage (2 kg/hectare) of Metoxuron alone under otherwise identical conditions. The degree of dessication of the potato haulms as a function of time in each case is determined. In each case an acceleration of the effect of Metoxuron was noted when applied in admixture with each of the following activators.

N,N-dimethyloctadecylamine $nC_{18}H_{37}N(CH_3)_2$
dihexylamine $NH(nC_6H_{13})_2$
dicyclohexylamine $NH(C_6H_{11})_2$
dibenzylamine $NH(CH_2C_6H_5)_2$
dioctadecylamine $NH(nC_{18}H_{37})_2$
ditridecylamine $NH(nC_{13}H_{27})_2$
di-undecylamine $NH(nC_{11}H_{23})_2$
N-*t*-butylcyclohexylamine $(C_6H_{11})NH(tC_4H_9)$
N-ethyl-1-naphthylamine 
dimethyldocosanylamine $nC_{22}H_{45}N(CH_3)_2$
dimethyl soya fatty amine $nC_4H_9(CH{=}CH)_2{-}(CH_2)_8N(CH_3)_2$
N,N-dimethylcyclohexylamine 
N,N-dimethyl-1-naphthylamine 
6-diethylamino-1-hexyne $HC{\equiv}C(CH_2)_4N(C_2H_5)_2$
di-dodecylamine $(C_{12}H_{25})_2NH$
N-methyl-di-octadecylamine $(C_{18}H_{37})_2NCH_3$
N-methyl-di-dodecylamine $(C_{12}H_{25})_2NCH_3$
triallylamine $N(CH_2CH{=}CH_2)_3$
N-methyl-dodecylamine $(C_{12}H_{25})NH(CH_3)$
N-*n*-butyl-dodecylamine $(C_{12}H_{25})NH(nC_4H_9)$
N-ethyl-tetradecylamine $(C_{14}H_{29})NH(C_2H_5)$
tri-n-octylamine $N(C_8H_{17}n)_3$ and its phosphate
tri-n-octylamine in phosphate salt form
tri-*i*-octylamine $N(C_8H_{17}i)_3$
tri-(2-ethylhexyl)methylammonium chloride
tri-*i*-nonylamine $N(C_9H_{19}i)_3$
tri-*n*-decylamine $N(C_{10}H_{21}n)_3$
tri-*n*-dodecylamine $N(C_{12}H_{25}n)_3$
tri-hydrogenated tallow amine
tri-oleylamine $[CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2]_3N$
tri-amylamine $N(C_5H_{11}n)_3$
tri-*n*-hexylamine $N(C_6H_{13}n)_3$
tri-*n*-heptylamine $N(C_7H_{15}n)_3$
tri-2-ethylhexylamine $N[CH_2CH(C_4H_9n)C_2H_5]_3$
tri-*i*-pentylamine $N[CH_2CH(CH_3)C_2H_5]_3$
tri-benzylamine $N(CH_2C_6H_5)_3$
n-octyldimethylamine $(nC_8H_{17})N(CH_3)_2$

dioctylamine $NH(nC_8H_{17})_2$
N,N-dioctylmethylamine $(CH_3)N(C_8H_{17}n)_2$
N,N-dibutyl-2-ethylhexylamine $(nC_4H_9)_2NCH_2CH(C_2H_5)nC_4H_9$
N-methyl-di-2-ethylhexylamine $CH_3N[CH_2CH(C_2H_5)(C_4H_9n)]_2$
N,N-dimethyl-di-2-ethylhexylamine $(CH_3)_2N[CH_2CH(C_2H_5)(C_4H_9n)]$
N-*n*-butyl-di-2-ethylhexylamine $(nC_4H_9)N[CH_2CH(C_2H_5)(C_4H_9n)]_2$
bis-(2-ethylhexyl)-amine $HN[CH_2CH(C_2H_5)(C_4H_9n)]_2$
lauryldimethylamine $(nC_{12}H_{25})N(CH_3)_2$
n-tetradecyldimethylamine $(n\text{-}C_{14}H_{29})N(CH_3)_2$
decyldimethylamine $(nC_{10}H_{21})N(CH_3)_2$
palmityldimethylamine $(nC_{16}H_{33})N(CH_3)_2$
dimethyloleylamine $CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2N(CH_3)_2$
tributyl phosphate
tributoxyethyl phosphate (technical mixture of dibutyl hydrogen phosphate and butyl dihydrogen phosphate; BAP; Albright and Wilson Ltd.)
butyl acid phosphate
butyl acid phosphate in ammonium salt form
butyl acid phosphate in sodium salt form
di(2-ethylhexyl)phosphoric acid
tributyl citrate
diethyl phthalate
dibutyl phthalate
dibutyl sebacate
butyl oleate
dioctyl phthalate
and triphenyl phosphate.

When Metoxuron is replaced by the following compounds, a similar effect is observed:
3-(3-chloro-4-methylphenyl)-1,1-dimethyl urea (chlorotoluron)
3-(3,4-dichlorophenyl)-1,1-dimethyl urea (diuron)
2-(chloro-4-ethylamino-6-isopropylamino-*S*-triazine (atrazine)
2-chloro-4,6-bis(ethylamino)-*s*-triazine (simazine)

Examples of emulsifiable concentrates of the activators suitable for use in Example 1 are:

Ex.	Activator	Emulsifier/Surfactant	Other ingredients (solvent)
2	50% Trioctylamine	15% Atlox 4851B	35% isopropanol
3	32% Trioctylamine phosphate	7.5% Atlox 4851B	60.5% isopropanol
4	62% Trihexylamine	10% emulsifier (5 parts Tween 80 + 3 parts Span 20)	28% isopropanol
5	76.5% active ingredient in Aliquat 336	23.5% Atlox 3400B	–
6	85% Tri-n-butyl-phosphate	15% Atlox 4851B	–
7	80% Tri-butoxy-ethyl-phosphate	5% emulsifier (3.25 parts Tween 80 + 1.75 parts Span 20)	15% xylene
8	44.5% Tri-n-octyl-phosphin oxide	16.6% emulsifier (1 part Atlox 4851B + 1 part Atlox 3500B)	38.9% xylene
9	26.3% 4-Nonylphenol	5% sodium lauryl sulphate (surfactant)	36.6% xylene 32.1% dimethylformamide
10	55.9% Di-(2-ethylhexyl)-phosphoric acid	9% Atlox 4851B	35.1% isopropanol

– Atlox 4851B, Atlox 3400B, Atlox 3500B, Tween 80 and Span 20 of the firm Atlas Chem. Co., now I.C.I. Atlas.
– Aliquat 336 (Methyl tri-caprilyl ammonium chloride) of the firm General Mills Inc.
– 4-Nonylphenol of the firm J. T. Baker Chemicals.

EXAMPLE 11

The tank mix employed in Example 1 is produced by suspending 1.25 (or 2.5) kg Purivel and 5 kg of an 80% emulsifiable concentrate of a activator (e.g. tributylphosphate) in 500 l of water.

The activator emulsifiable concentrate is produced as follows:

80 parts of activator, e.g. tributylphosphate
2.5 parts of polyoxyethylated sorbitan mono-oleate
2.5 parts of sorbitan monolaurate
and 15 parts xylene
are mixed until a clear preparation easily emulsifiable in water is obtained.

EXAMPLE 12

In a manner analogous to Example 11, the following emulsifiable concentrate is obtained:

12.25% Metoxuron (techn. 98% active ingredient)
60% Tri-n-butylphosphate
10% emulsifier (2 parts Atlox 3400 B and 3 parts Atlox 4855B)
10% Cyclohexanone
7.75% Dimethylformamide.

The so obtained emulsifiable concentrate, containing 120 g/l Metoxuron and 600 g/l tri-n-butylphosphate, is applied at a rate of 5 l/hectare of crop.

EXAMPLE 13

In a manner analogous to Example 11, the following emulsifiable concentrate is obtained:

26.3% 4-Nonylphenol (of the firm J. T. Baker Chem.)
33.2% Xylene
25% Dimethylformamide
10.5% Metoxuron (techn. 98% active ingredient)
5% surfactant (sodium lauryl sulphate).

The so obtained emulsifiable concentrate, containing 100 g/l Metoxuron and 250 g/l 4-nonylphenol, is applied at a rate of 10 l per hectare of crop.

EXAMPLE 14

Instead of the tank mix employed in Example 1, the following 50% wettable powder may be employed:

10.5 parts herbicide, e.g. Metoxuron (technical grade)
40 parts activator, e.g. tribulylphosphate
2 parts sodium lauryl sulphate
2 parts lignin sulphonate
and 45.5 parts silica

The formulation is produced by spraying the plasticiser onto the silica to form a dry powder, mixing with sodium lauryl sulphate, lignin sulphonate and herbicide in a blender and milling the mixture until the particule size is substantially below 30 microns.

EXAMPLE 15

Instead of the tank mix employed in Example 1, the following 40% wettable powder may be employed:

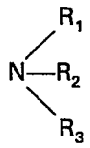
8% Metoxuron
32% Tri-n-octylamine
8% surfactant (Tensiofix EDS of the firm Tensia S.A. Liège, Belgium)
40% Silica
10% Kaolin
2% Lignin sulphonate.

The formulation is produced by mixing tri-n-octylamine and the surfactant, spraying this mixture onto the silica to form a dry powder, mixing this with Metoxuron, kaolin and lignin sulphonate in a Wareing blender and milling it to form a wettable powder containing 80 g/kg Metoxuron and 320 g/kg tri-n-octalamine. The wettable powder is applied at a rate of 6.25 kg/hectare of crops.

CLAIMS

1. A method of defoliating crops which comprises applying to the crops a defoliating aggregate amount of
a) a herbicide and
b) an activating amount of a solvent used in the metallurgic industry for the extraction of metals.
2. A method according to Claim 1, wherein the herbicide is a herbicide phenyl urea.
3. A method according to Claim 1, wherein the herbicide is a herbicide triazine.
4. A method according to Claim 2, wherein the herbicide is 3-(3-chloro-4-methoxyphenyl)-1,1-dimethyl urea.

5. A method according to any one of the preceding claims wherein the solvent as used in the metallurgic industry for the extraction of metals is an amine of formula I,



I

wherein R_1 and R_2 are each, independently, a C_{1-24}hydrocarbon group,
and R_3 is hydrogen or a C_{1-24}hydrocarbon group,
in free base or in agriculturally acceptable ammonium or in quaternary ammonium salt form.

6. A method according to Claim 5, wherein the amine is tri-n-hexyl amine.

7. A method according to Claim 5, wherein the amine is tri-caprilyl amine.

8. A method according to Claim 7, wherein tri-caprilyl amine is in the methyl ammonium chloride form.

9. A method according to Claim 5, wherein the amine is tri-n-octyl amine.

10. A method according to Claim 8, wherein the tri-n-octyl amine is in the phosphate salt form.

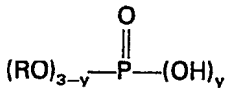
11. A method according to any one of the preceding Claims 1 to 4, wherein the solvent as used in the metallurgic industry for the extraction of metals is a plasticizer for polymers.

12. A method according to Claim 11, wherein the plasticizer for polymers is a compound of formula II,

$$(RO)_x—A \qquad II$$

wherein each R is independently C_{1-12}alkyl, C_{2-12}alkoxy-alkyl or phenyl,
A is an acyl residue of any aliphatic or aromatic carboxylic acid or of phosphoric acid,
and x is an integer 1 to 3 being the number of free valencies of the phosphoric acid ester or the carboxylic acid residue.

13. A method according to Claim 12, wherein the plasticizer is a compound of formula IIa,



IIa

wherein R is as defined above,
and y is 0, 1 or 2.
in free base or in agriculturally acceptable salt form.

14. A method according to Claim 13, wherein the plasticizer is tri-butylphosphate.

15. A method according to Claim 13, wherein the plasticizer is tri-butoxyethyl phosphate.

16. A method according to Claim 13, wherein the plasticizer is butyl acid phosphate.

17. A method according to any one of the preceding Claims wherein the herbicide is applied at a rate of 0.5 to 4.0 kg per hectare of crop and the weight ratio of activator/herbicide is in the range 0.5—5:0.5—4.

18. A composition for the defoliation of crops comprising a defoliating aggregate amount of a herbicide and an activating solvent as defined in any one of Claims 1 to 16.

19. A composition according to Claim 18, wherein the weight ratio activating solvent:herbicide is in the range 1—3:0.5—2.

20. A composition according to Claim 19, wherein the weight ratio activating solvent of formula I herbicide is 1—3:0.5—2.

21. A composition according to Claim 19, wherein the weight ratio activating solvent of formula II: herbicide is 2—5:1.

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